Effect of pressure on the superconductivity of $Rb_{0.19}WO_3$

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Abstract

We have performed electrical resistivity measurements under pressures up to 20GPa between 1 and 300K on monocrystalline hexagonal $Rb_{0.19}WO_3$. For pressures lower than ~5GPa, we observe a decrease of the metallic-like resistivity at room temperature as well as a small decrease of T_c. At this pressure, the resistivity starts to increase slowly up to 10GPa accompanied by a sharper decrease of T_c .The resistivity curves above 10GPa denote an activated behaviour and a T_c lower than 3K indicating that there is a phase transition that takes place gradually between 5 and 10GPa. We interpret our measurements as the result of structural transformations under high pressure.

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Pressure; Superconductivity; Phase transitions; oxides

1. Introduction

The study of tungsten bronzes was given a strong momentum after the report of evidence for surface superconductivity with a superconducting transition temperature T_c of the order of 100K [1,2,3,4]. Tungsten bronzes have been intensively studied in the past due to its highly soft perovskite structure that induces a strong interaction between carriers and soft phonons leading to polaron and bipolaron formation [5]. The bulk structure of WO_3 corresponds to a tetragonal lattice formed by WO_6 octahedra that can be stacked into a ABO_3 perovskite structure with the W occupying the B sites and with the A site being empty. Band structure calculations [6] have shown that the material is a semiconductor with a gap of around 1eV (though experimental optical gaps are higher [7], indirect gap = 2.5eV), with the valence bands originating mainly from O 2*p* orbitals and the conduction bands from W*d* ones. Reduction of the compound results in a small oxygen non-stoichiometry and conducting samples. The stoichiometric material shows thermally activated hopping conductivity with activation energies between 0.15 and 0.27 eV, depending on the crystal quality [8,9,10,11]. At temperatures below 130K there is a change to a regime with much smaller activation energies. At even lower temperatures the electrical conductivity becomes nearly temperature independent as expected by hopping small polaron conduction affected by disorder[12]. In non-stoichiometric samples bipolarons[5] are observed for carrier concentrations <3.7x1021 cm-1. On the other hand, sheet superconductivity at 3K in reduced WO_3 was also reported [13]. Though the superconducting structure is unknown [14], the behaviour of the electrical resistivity, obviously the result of the carriers at the origin of the superconducting transition, is abnormal with an activated region at low temperatures.

Carriers can be introduced also by alcaline ion intercalation. Structural changes occur together with the superconducting properties expected for such strong electron-phonon interaction materials. In particular the case of Rb intercalation generates hexagonal tungsten bronzes, with form 3- and 6-membered rings, leaving trigonal and hexagonal channels along the c axis. The radius of the hexagonal cavities is ~2Å. These materials are superconducting with T_c's that can reach 7K[15]. Their properties can be very complex and different reports have claimed some rather different normal transport properties [16]. Recently, doping with oxygen replacement by fluorine[17] has yielded the compound $WO_{2.6}F_{0.4}$ with a T_c=0.4K.

2. Experimental

The samples we studied have been obtained by acid etching stoichiometric single crystals to reduce their Rb content. The $Rb_{0.33}WO_3$ crystals were grown electrolytically from a melt consisting of Rb_2CO_3 and WO_3-according to the method developed by Sienko and Morehouse[18]. The homogeneity of the samples and the final x value (0.195 ± .01) was checked by measuring the magnetic anomaly associated with the superconducting transition (T_c = 5.5 K at ambiant pressure) and confirmed by a micro-probe analysis.

The electrical resistivity measurements were performed in a sintered diamond Bridgman anvil apparatus using a pyrophillite gasket and two steatite disks as the pressure medium. The Cu-Be device that locked the anvils can be cycled between 4.2K and 300K in a sealed dewar. The overall uncertainty in the quasi-hydrostatic pressure is estimated to be ±15%. The pressure spread across the sintered diamond anvils was previously determined on Pb-manometers to be of about 1.5-2GPa depending on the applied pressure, through the measurement of the superconducting transition temperature of Pb at low temperatures. The temperature was determined using calibrated Cernox thermometer with a maximum uncertainty (due mainly to temperature gradients across the Cu-Be clamp) of 0.5K. Four probes electrical resistivity d.c. measurements were made using a Keithley 2182 nanovoltmeter combined with a Keithley 238 current source and by using platinum wires to make contacts on the sample.

3. Results

We show on Fig. 1 the electrical resistance as a function of temperature for different pressures. We observe that for the first pressures there is an irreversibility of the curves : the up curves show an increase of the resistance that results in a bump. Behaviour similar to this has been reported by Stanley et al. [16] who attributed it to a phase transition, that can be a charge density wave (CDW), an ordering of the alkaline, or a coupled version of both phenomena, as in some organic compounds[19]. With increasing pressures, the irreversibilities become less visible and are totally inexistent in the curves obtained at 4 GPa.

As pressure is increased we note a change in the temperature dependence of the resistivity : it passes from a metallic behaviour to an activated, i.e. increasing with decreasing behaviour. It is clear that there are important changes in the sample, possibly a phase transition under pressure. A lattice distortion has been reported in $Rb_{0.31}WO_3$ [20] for pressures higher than 2GPa : the octahedra that form the channel tilt around the c axis of the lattice. Considering that our pressure gradient is of about 2GPa (as determined by the width of the superconducting transitions of Pb manometers), the transition temperature reported for this distortion coincides with the disappearance of the irreversibilities. It may thus explain why we do not see the apparent ordering of the Rb atoms at 4GPa, as the tilted octahedra can impede the normal displacements of the Rb atoms along the channels. It is possible that as pressure is increased different or more pronounced distortions of the structure may appear in this soft lattice.

We show on Fig. 2 a detail of the superconducting transitions. The transition temperature decreases as a function of pressure as shown on Fig. 3. It is clear that there is a structural phase transition between 5 and 10GPa, as both the resistance at 10K and T_c show a significant change around this pressure. It is interesting to note that both the T_c and the resistance curves at the higher pressures look very much like those of superconducting [13] reduced WO_3. The activated behaviour does not seem to indicate that the material has become semiconducting as, it that case we would expect an insulator at low temperatures, not a superconductor. We have verified that the superconducting transition is due to the whole of the sample by testing the critical currents at the foot of the superconducting transition. These were of the same order of magnitude for the sample at low pressures and the sample at high pressures (filamentary superconductivity would have yielded much smaller critical currents.

4. Discussion

The picture that evolves from our results seems to be the following. At low pressures, we observe irreversibilities in the electrical resistance with pressure that are most probably due to an hysteretic ordering of the Rb atoms. As the material undergoes the pressure-induced distortion [20], the Rb atoms are pinned down by them, and can no longer move along the channels. As a consequence, the carriers that coupled to the Rb ordering are now also pinned down by the static Rb atoms, and can only conduct by activated hopping. We thus expect a 3D variable range hopping ($\exp\left[(T_0/T)^{1/4}\right]$) or a polaronic ($T \cdot \exp\left[T_H/T\right]$) type conductance or eventually a plain semiconducting type ($\exp\left[\Delta_H/T\right]$). There are clearly two régimes for the electrical resistance, first one above ~60K and a second one between this temperature and the superconducting transition. We have not been able to fit the high temperature régimes for the different pressures with any of the mentioned dependences. In the low temperature régime, the fit with the largest temperature range (20K) corresponds to the plain semiconducting type ($\exp\left[\Delta_H/T\right]$)However, the gap values obtained are too small for an actual semiconductor, ~ one tenth of k_BT. Thus, another interpretation is necessary for this dependence. Obviously it would be interesting to confirm the phase transition around 10GPa with crystallographic measurements under pressure, in order to determine the distortion involved.

5. Conclusions

Our pressure measurements show at low pressures an irreversibility of the electrical resistance, most probably due to an ordering of Rb atoms at low temperatures. At about 10GPa there is a transition to another phase with a lower T_c=3K. The proposed new high pressure phase shows in the electrical resistance an activated behaviour, that is flattened at around 25K towards an apparent Arrhenius behaviour. Further theoretical and experimental studies are needed to understand the origin of the unusual pre-transitional behaviour in $Rb_{0.19}WO_3$.

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Figures

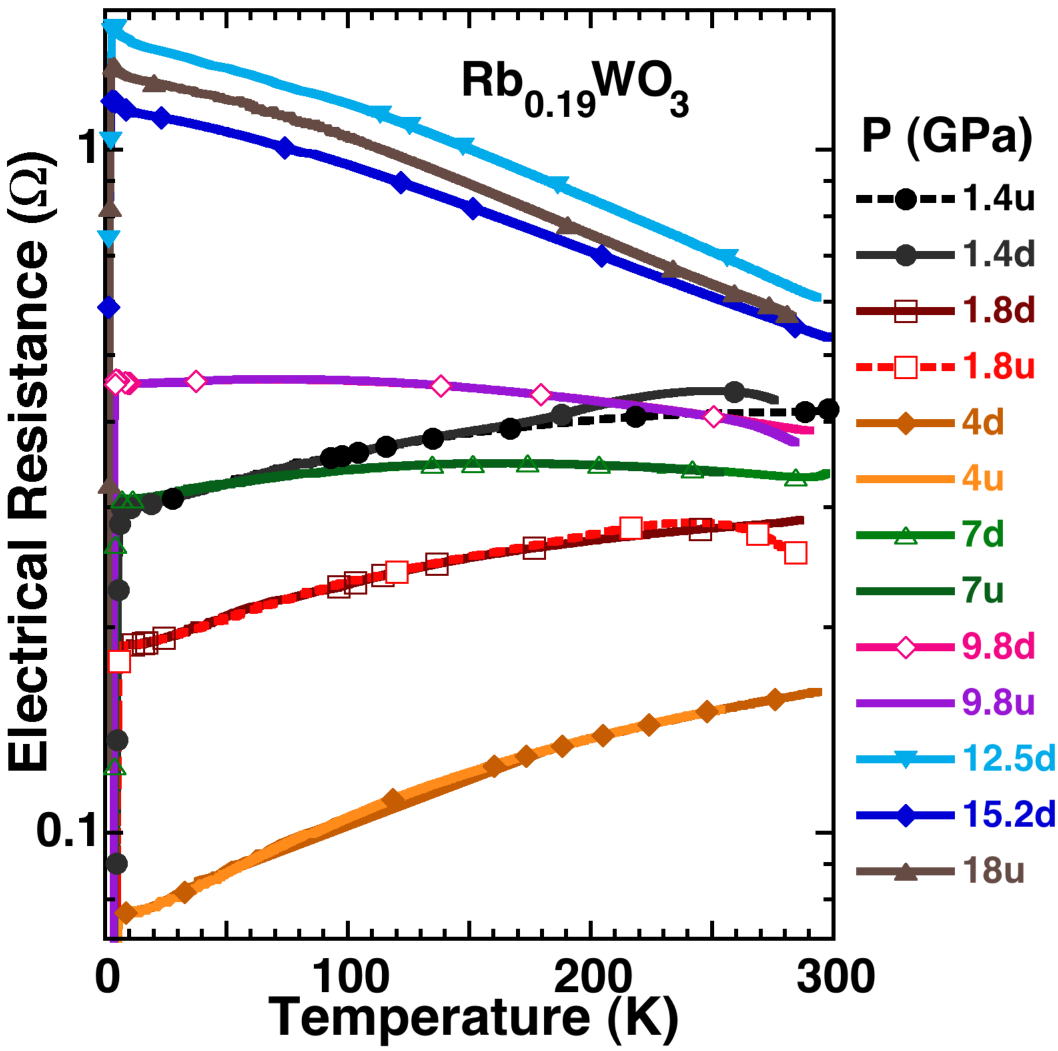

Figure 1

Electrical resistance of a $Rb_{0.19}WO_3$ monocrystal as a function of temperature for several pressures. The terms d and u correspond to data taken on cooling or on heating. We observe that only for the two lowest pressures there is an irreversibility, probably due to the ordering of the non-stoichiometric Rb atoms at low temperature. We note that the high pressure curves show an activated behaviour.

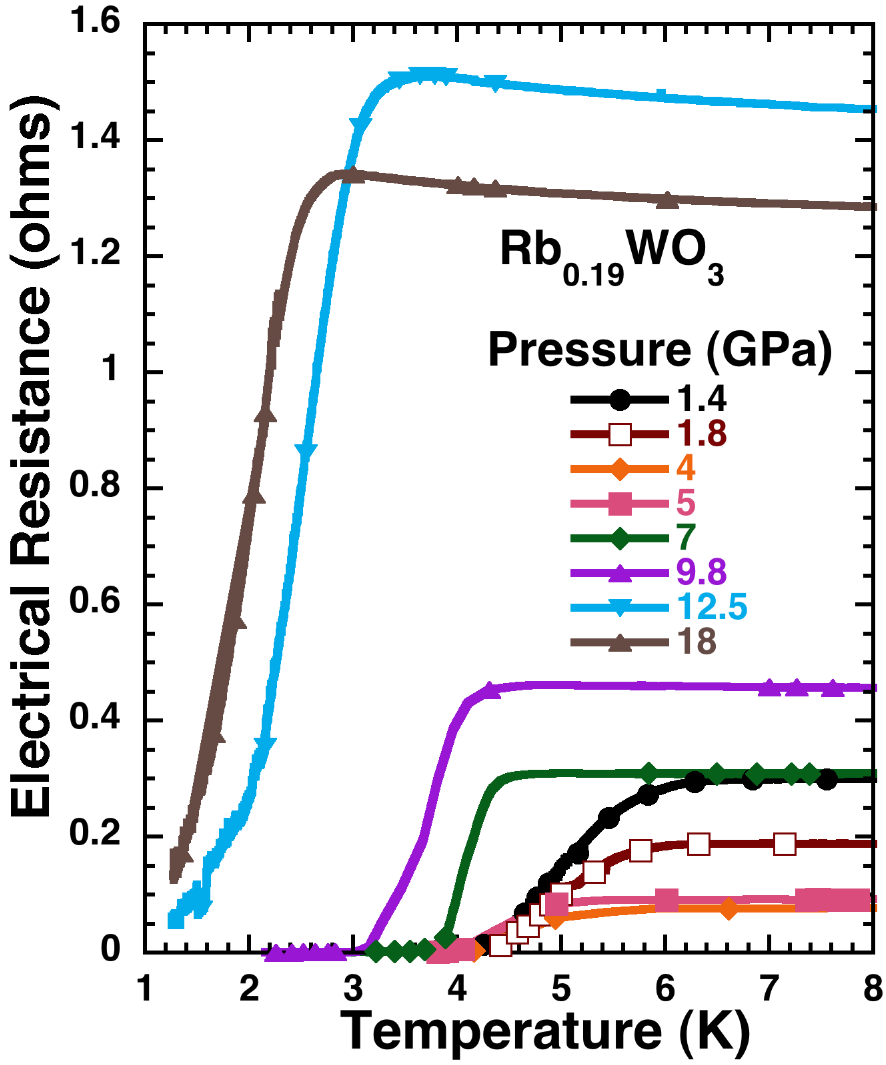

Figure 2

Detail of the superconducting transition at low temperature

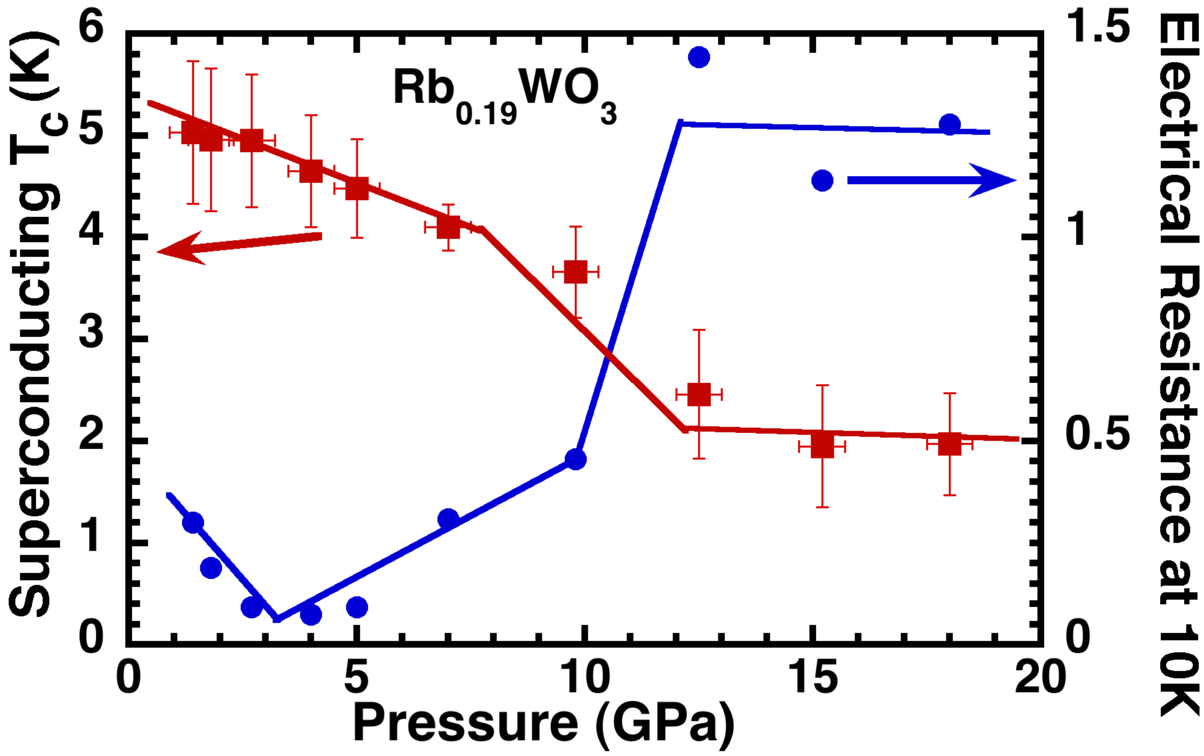

Figure 3

Pressure dependence of the superconducting transition temperature T_c and of the value of the resistance at 10K. It is clear that a transition, probably a structural distortion, happens

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